

THE CLAIMS

What is claimed is:

1. A composition for removing silicon-containing particulate material from the surface of a semiconductor wafer, said composition comprising a supercritical fluid (SCF), at least one co-solvent, at least one etchant species, at least one surface passivator, a binder interactive with said silicon-containing particulate material to enhance removal thereof, deionized water, and optionally at least one surfactant.
2. The composition of claim 1, wherein the SCF is selected from the group consisting of carbon dioxide, oxygen, argon, krypton, xenon, and ammonia.
3. The composition of claim 1, wherein the SCF comprises carbon dioxide.
4. The composition of claim 1, wherein the co-solvent comprises at least one solvent selected from the group consisting of alkanols, dimethylsulfoxide, sulfolane, catechol, ethyl lactate, acetone, butyl carbitol, monoethanolamine, butyrol lactone, alkyl carbonates, glycol amines, or a mixture of two or more of such species.
5. The composition of claim 1, wherein the co-solvent comprises at least one C₁-C₆ alcohol.
6. The composition of claim 1, wherein the co-solvent comprises methanol.
7. The composition of claim 1, wherein the silicon-containing particulate material comprises silicon nitride.

8. The composition of claim 1, wherein the silicon-containing particulate material comprises silicon oxide.
9. The composition of claim 1, wherein the etchant species is selected from the group consisting of hydrofluoric acid, ammonium fluoride, triethylamine trihydrofluoride and bifluoride salts.
10. The composition of claim 9, wherein the etchant species comprises ammonium fluoride.
11. The composition of claim 1, further comprising a surfactant.
12. The composition of claim 11, wherein the surfactant comprises at least one nonionic surfactant selected from the group consisting of fluoroalkyl surfactants, ethoxylated fluorosurfactants, polyethylene glycols, polypropylene glycols, polyethylene ethers, polypropylene glycol ethers, carboxylic acid salts, dodecylbenzenesulfonic acid, dodecylbenzenesulfonic salts, polyacrylate polymers, dinonylphenyl polyoxyethylene, silicone polymers, modified silicone polymers, acetylenic diols, modified acetylenic diols, alkylammonium salts, modified alkylammonium salts, and combinations comprising at least one of the foregoing.
13. The composition of claim 11, wherein the surfactant comprises at least one anionic surfactant selected from the group consisting of fluorosurfactants, sodium alkyl sulfates, ammonium alkyl sulfates, alkyl (C₁₀-C₁₈) carboxylic acid ammonium salts, sodium sulfosuccinates and esters thereof, and alkyl (C₁₀-C₁₈) sulfonic acid sodium salts.

14. The composition of claim 11, wherein the surfactant comprises an ethoxylated fluorosurfactant.
15. The composition of claim 1, wherein the interactions between the binder and the silicon-containing particulate material comprise intermolecular interactions selected from the group consisting of hydrogen bonding and van der Waals forces.
16. The composition of claim 1, wherein the binder comprises a polymeric alcohol derived from at least one ethylenically unsaturated reactant.
17. The composition of claim 1, wherein the binder comprises polyvinyl alcohol.
18. The composition of claim 1, wherein the binder comprises a polymeric amine derived from at least one ethylenically unsaturated reactant.
19. The composition of claim 1, wherein the binder comprises polyvinyl amine.
20. The composition of claim 1, wherein the interactions between the binder and the silicon-containing particulate material reduce the silicon-containing particulate material count on the surface of the semiconductor wafer.
21. The composition of claim 1, wherein the surface passivator is selected from the group consisting of boric acid, triethyl borate and triethanolamine.
22. The composition of claim 1, wherein the surface passivator comprises boric acid.

23. The composition of claim 1, wherein the composition comprises about 75.0% to about 99.9% SCF, about 0.05% to about 22.5% co-solvent, about 0.01% to about 5.0% etchant, about 0.01% to about 1.25% surface passivator, about 0.01% to about 3.75% binder, 0% to about 1.25% surfactant and about 0.01% to about 3.5% deionized water, based on the total weight of the composition.

24. The composition of claim 23, wherein the ratio of etchant to surface passivator is about 2:3 to about 4:3.

25. A method of removing silicon-containing particulate matter from a semiconductor wafer surface having same thereon, said method comprising contacting the wafer surface with a SCF-based composition comprising a SCF, at least one co-solvent, at least one etchant species, at least one surface passivator, a binder interactive with said silicon-containing particulate material to enhance removal thereof, deionized water, and optionally at least one surfactant, for sufficient time and under sufficient contacting conditions to remove the silicon-containing particulate matter from the surface of the semiconductor wafer.

26. The method of claim 25, wherein the SCF is selected from the group consisting of carbon dioxide, oxygen, argon, krypton, xenon, and ammonia.

27. The method of claim 25, wherein the SCF comprises carbon dioxide.

28. The method of claim 25, wherein the contacting conditions comprise pressures in a range of from about 1200 to about 4500 psi.

29. The method of claim 25, wherein said contacting time is in a range of from about 4 minutes to about 20 minutes.

30. The method of claim 25, wherein the co-solvent comprises at least one solvent selected from the group consisting of alkanols, dimethylsulfoxide, sulfolane, catechol, ethyl lactate, acetone, butyl carbitol, monoethanolamine, butyrol lactone, alkyl carbonates, glycol amines, or a mixture of two of more of such species.

31. The method of claim 25, wherein the co-solvent comprises at least one C₁-C₆ alcohol.

32. The method of claim 25, wherein the silicon-containing particulate matter comprises silicon nitride.

33. The method of claim 25, wherein the silicon-containing particulate matter comprises silicon oxide.

34. The method of claim 31, wherein the silicon nitride particles are generated during plasma-enhanced chemical vapor deposition (PECVD) of a silicon-containing material at the semiconductor wafer surface.

35. The method of claim 25, wherein the etchant species is selected from the group consisting of hydrofluoric acid, ammonium fluoride, triethylamine trihydrofluoride and bifluoride salts.

36. The method of claim 25, wherein the etchant species comprises ammonium fluoride.

37. The method of claim 25, further comprising a surfactant.
38. The method of claim 37, wherein the surfactant comprises at least one nonionic surfactant selected from the group consisting of fluoroalkyl surfactants, ethoxylated fluorosurfactants, polyethylene glycols, polypropylene glycols, polyethylene ethers, polypropylene glycol ethers, carboxylic acid salts, dodecylbenzenesulfonic acid, dodecylbenzenesulfonic salts, polyacrylate polymers, dinonylphenyl polyoxyethylene, silicone polymers, modified silicone polymers, acetylenic diols, modified acetylenic diols, alkylammonium salts, modified alkylammonium salts, and combinations comprising at least one of the foregoing.
39. The method of claim 37, wherein the surfactant comprises at least one anionic surfactant selected from the group consisting of fluorosurfactants, sodium alkyl sulfates, ammonium alkyl sulfates, alkyl (C₁₀-C₁₈) carboxylic acid ammonium salts, sodium sulfosuccinates and esters thereof, and alkyl (C₁₀-C₁₈) sulfonic acid sodium salts.
40. The method of claim 25, wherein the interactions between the binder and the silicon-containing particulate material comprise intermolecular interactions selected from the group consisting of hydrogen bonding and van der Waals forces.
41. The method of claim 25, wherein the binder comprises a polymeric alcohol derived from at least one ethylenically unsaturated reactant.
42. The method of claim 25, wherein the binder comprises polyvinyl alcohol.

43. The method of claim 25, wherein the binder comprises a polymeric amine derived from at least one ethylenically unsaturated reactant.
44. The method of claim 25, wherein the binder comprises polyvinyl amine.
45. The method of claim 41, wherein the polymeric alcohol adsorbs to silazane ($\text{Si}_2\text{-NH}$) and/or silanol (Si-OH) groups at the surface of the silicon-containing particulate material.
46. The method of claim 25, wherein the surface passivator is selected from the group consisting of boric acid, triethyl borate and triethanolamine.
47. The method of claim 25, wherein the surface passivator comprises boric acid.
48. The method of claim 25, wherein the SCF-based composition comprises about 75.0% to about 99.9% SCF, about 0.05% to about 22.5% co-solvent, about 0.01% to about 5.0% etchant, about 0.01% to about 1.25% surface passivator, about 0.01% to about 3.75% binder, 0% to about 1.25% surfactant and about 0.01% to about 3.5% deionized water, based on the total weight of the composition.
49. The method of claim 25, wherein the contacting step comprises a cycle including (i) dynamic flow contacting of the SCF-based composition with the wafer surface containing the silicon-containing particulate material, and (ii) static soaking contacting of the SCF-based composition with the wafer surface containing the silicon-containing particulate material.

50. The method of claim 49, wherein said cycle comprises alternatingly and repetitively carrying out dynamic flow contacting and static soaking contacting of the wafer surface containing the silicon-containing particulate material.

51. The method of claim 25, wherein the contacting conditions comprise temperatures in a range from about 30°C to about 100°C.

52. The method of claim 25, wherein the contacting conditions comprise temperatures in a range from about 40°C to about 70°C.

53. The method of claim 25, further comprising the step of washing the wafer surface, at a region at which the silicon-containing particulate material have been removed, with a SCF/methanol/deionized water wash solution in a first washing step, and with a SCF in a second washing step, to remove residual precipitated chemical additives in said first washing step, and to remove residual precipitated chemical additives and/or residual alcohol in said second washing step.

54. The method of claim 53, wherein the SCF is SCCO_2 .

55. A composition for removing silicon-containing particulate material from the surface of a semiconductor wafer, said composition comprising about 85.0% to about 99.0% SCF, about 0.01% to about 15.0% co-solvent, about 0.25% to about 5.0% etchant, and optionally about 0% to about 3.0% surfactant, based on the total weight of the composition.

56. A method of removing silicon-containing particulate matter from a semiconductor wafer surface having same thereon, said method comprising:

pre-cleaning the wafer surface with a SCF-based pre-cleaning composition comprising a SCF and an aqueous-based pre-cleaning formulation; and

contacting the wafer surface with a SCF-based composition comprising a SCF, at least one co-solvent, at least one etchant species, and optionally at least one surfactant, for sufficient time and under sufficient contacting conditions to remove the silicon-containing particulate matter from the surface of the semiconductor wafer.

57. The method of claim 56, wherein the aqueous-based pre-cleaning formulation comprises ammonium hydroxide, t-butyl hydrogen peroxide and water.

58. The method of claim 56, wherein the wafer surface is pre-cleaned in a pressure range from about 1200 psi to about 2900 psi.

59. The method of claim 56, wherein the wafer surface is pre-cleaned in a temperature range from about 40°C to about 60°C.